

THE OXIDATION OF CERTAIN
CYCLIC COMPOUNDS

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PREFACE

The problem involved in this dissertation may be divided into four sections. Each division constitutes a chapter of the dissertation.

The first chapter describes the fractionating equipment developed for the purification of terpenes and the analysis of reaction products.

The second chapter describes the oxidation of beta pinene by air, with and without catalyst, at various temperatures. The method for the separation of the products is given.

In the third chapter is given the electrochemical action of the pinenes in sulfuric acid and sodium bicarbonate emulsions, using platinum and lead dioxide anodes.

In the fourth chapter is given the electrochemical oxidation and selenium dioxide oxidation of cyclohexene.

The manner of listing references is the customary one for technical works in organic chemistry of comparable length and scope. Journal abbreviations are the official ones of the "Chemical Abstracts".

In conformity with present usage in research communications all temperatures are of the centigrade

scale, and the centigrade symbol is omitted.

The melting points are capillary melting points. The symbol "(Corr.)" is used after every corrected melting point. The thermometers used for obtaining the melting points were calibrated against a set of thermometers standardized by the Bureau of Standards.

Chapter I

FRACTIONATING COLUMNS

Introduction

Before any experimental work could be carried out with β -pinene, it had to be obtained as pure as possible. Since β -pinene forms no solid derivatives (51), it was obtained pure by the fractionation of commercial material.

Commercial β pinene is not pure but contains approximately 85% of this substance. It is obtained commercially from turpentine which is a complex mixture, consisting largely of terpene hydrocarbons (42 %) of the bicyclic mono-terpene series.

Since α pinene, the other main constituent of turpentine, and β -pinene do not have widely separated boiling points, it is necessary that efficient columns be used for their separation and purification. Many different types of efficient columns have been reported (36, 47). It has been found in this laboratory (56) that the spiral screen packed columns of Lecky and Ewell (33) are best for the purification of terpenes. However, the holdup of these analytical columns was too large for the successful analysis of the small

amounts of products which were sometimes obtained. A column with twisted wire packing as developed by Bower and Cooke (8) proved to be best suited for the analysis of these small quantities. An Ellis type receiver (14) does not permit sufficient flexibility of operation and hence another head and receiver was designed.

General Column Construction and Operation

The spiral steel columns were built as described by Fugitt, Stallcup and Hawkins (56) and the general assembly and operation were similar. The packing in the tube is surrounded by a concentric tube. This was wound by equally spaced nichrome wire so that 300 watts at 135 volts, instead of about 150 watts as used by the above authors. This was surrounded by a larger concentric tube for insulation and is called the air jacket.

The column was adjusted within two degrees of the head temperature by means of a transformer. A thermometer, which will be known as the column thermometer, was attached to the column so that it lay between the column and the heater jacket. Another thermometer, which will be known as the jacket thermometer was

Placed between the heater jacket and the air jacket and read about 90° when the column thermometer read 100° . The throughput was controlled by evaporation from the electrically heated pot. The heat on the pot was controlled by means of a transformer.

The theoretical plates were determined by the use of n-heptane methylcyclohexane mixtures and the data of Beatty and Calingaert (5) and Bromily and Quiggle (10). This was expressed as the H.E.T.P., which is the height equivalent to one theoretical plate.

The nondrainable holdup was measured by pouring a known weight of benzene through the packing and collecting the liquid drainings and reweighing. The column was allowed to drain for one minute. The difference in these weights gave the nondrainable holdup. This needs to be small for analytical work.

The operating holdup is the weight of liquid present in the column and head during a distillation. This was measured by the stearic acid method (58). A weighed amount of stearic acid was dissolved in a weighed amount of benzene and the mixture refluxed in the columns. When equilibrium was attained a sample was drawn from the kettle and weighed. The benzene was removed by evaporation on the steam

bath until constant weight resulted. From these two weighings the change in percent of stearic acid in the benzene remaining in the flask was calculated. Since the stearic acid is nonvolatile, its weight in the flask is constant, so the weight of benzene remaining in the flask could be calculated. The weight of benzene remaining subtracted from the weight originally present in the flask gives the operating holdup. The operating holdup divided by the number of theoretical plates gives the operating holdup per theoretical plate. Low operating holdup per theoretical plate gives sharper fractions and is necessary for the fractionation of small amounts of materials.

The pressure drop in the column was measured by connecting the manometer alternately to the head and kettle by means of a double diagonal stopcock. A small pressure drop is advantageous so that thermal reactions are a minimum in the kettle.

Column specifications, H.E.T.P. and other data are given in table I. Non drainable holdup, operating holdup and pressure drop are given in columns 1, 3 and 4 of table II

TABLE I

Specifications and H.E.T.P. of Stainless Steel Spiral Screen Columns

Column No.	Column Specifications	Observed n_{25}^D of liquid and vapor using n-heptane-methyleyclohexane mixture at throughput giving min. H.E.T.P.	Head	Kettle	Total No. of Plates	H. E. T. P. per inch
1	50 x 50 mesh stainless steel spiral screen I. D. 17 mm. Inner glass tube O.D. 6mm. Packing height 24 inches	1.3906		1.4180	62	0.39
2	50 x 50 mesh stainless steel spiral screen I. D. 17 mm. Inner glass tube O.D. 6 mm. Packing height 48 inches	1.3888		1.4178	78	0.61
3	60 x 60 mesh stainless steel spiral screen I. D. 11 mm. Inner nickel rod O.D. 2.5 mm. Packing Height 22 in.	1.3926		1.4106	36	0.63

TABLE II
Operating Characteristics of the Spiral Screen Columns at Atmospheric Pressure

Column No.	Nondrainable holdup (Benzene)	Throughput rate	Operating holdup	Pressure drop
1	24 g	90 cc/hr	35.8 g (atm)	--
		45 cc/hr		2 mm (at 20 mm)
		67 cc/hr		2.1 mm (at 20 mm)
2	12.5 g	90 cc/hr	19 g (atm.)	--
		45 cc/hr		1.0 mm (at 20 mm)
		90 cc/hr		1.4 mm (at 20 mm)
3	24.4 g	45 cc/hr	5.8 g (atm.)	--
		45 cc/hr		1.4 mm (at 20 mm)
		90 cc/hr		1.9 mm (at 20 mm)

Efficiency at Various Rates of Throughput

In order to establish optimum conditions in actual fractionations, it was necessary to determine the variation in H.E.T.P. with rate of throughput at total reflux.

The column temperature was adjusted to within two degrees of the head temperature and the throughput was controlled by evaporation from electrically heated kettles. If the column is so long that the bulb of the column thermometer is more than ten inches from the bottom of the column, it was found that the column operates most efficiently at a temperature of about 2° below the head temperature. If the column is so short that the bulb of the column thermometer is within two or three inches of the bottom of the column, then the column operates most efficiently when the thermometer reads about 2° above the head temperature.

n-Heptane methylcyclohexane mixtures were used to make the following determinations. The throughput was determined by counting the drops returned through the drop counter to the column under total reflux. Fig I is a diagram of the head used, and the drop return, A, was calibrated by adding a methylcyclohexane n-heptane mixture to the top of the head in such a way that it

would run down the side of the condenser and through the drop counter into a graduated cylinder.

It was found that if the exposed parts of the kettle and head were not insulated the column efficiency was reduced as much as one half. Insulation was effected by wrapping the exposed parts with glass wool.

Efficiencies at various throughput rates are given in table III, page 13.

Efficiencies at Optimum Throughput Rate at Various Reflux Ratios

The ability of a fractionating column to separate a mixture depends upon several factors, the most important of which are relative volatility of the components, the number of theoretical plates and the reflux ratio at which the product is collected. The magnitude of the effect of the reflux ratio in any given case depends upon the vapor pressure ratio of the components, and the total equivalent plates at total reflux as well as the reflux ratio. The order of importance of these is generally relative volatility, reflux ratio, and equivalent plates (46).

Reflux ratio is defined as the ratio of product returned to the column to the product collected; thus if in a period of time 20 cc of head reflux is returned to the column to 1 cc of head reflux collected as

product the reflux ratio is 20 : 1. Since no product can be collected at total reflux a portion of the head reflux must be collected as product in any fractionation. This lowers the efficiency of the fractionating column (3). It is desirable to know the reflux ratio best suited for the separation of the constituents of a mixture, hence the H.E.T.P. has been determined at several reflux ratios using the methylcyclohexane-n-heptane mixture. These data are given in table IV, page 14, and plotted in Fig. 2, page 15. The amount of material in the kettle was made large so that there would be little change in the kettle composition throughout the determination. The throughput was regulated to optimum conditions and the reflux ratio was adjusted by partially opening a diagonal adjustable flow stopcock. The drip point, F, (Fig. 1, page 12.) was calibrated in a manner similiar to the method used for the head return already described on page 9.

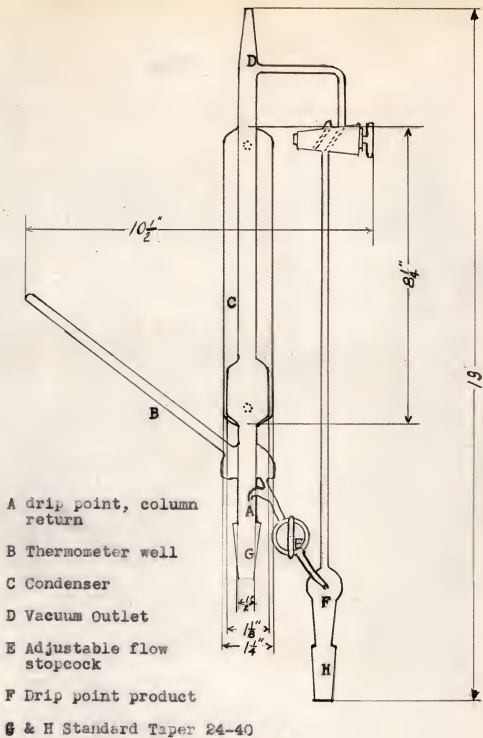


Fig. 1 Distilling Head

TABLE III

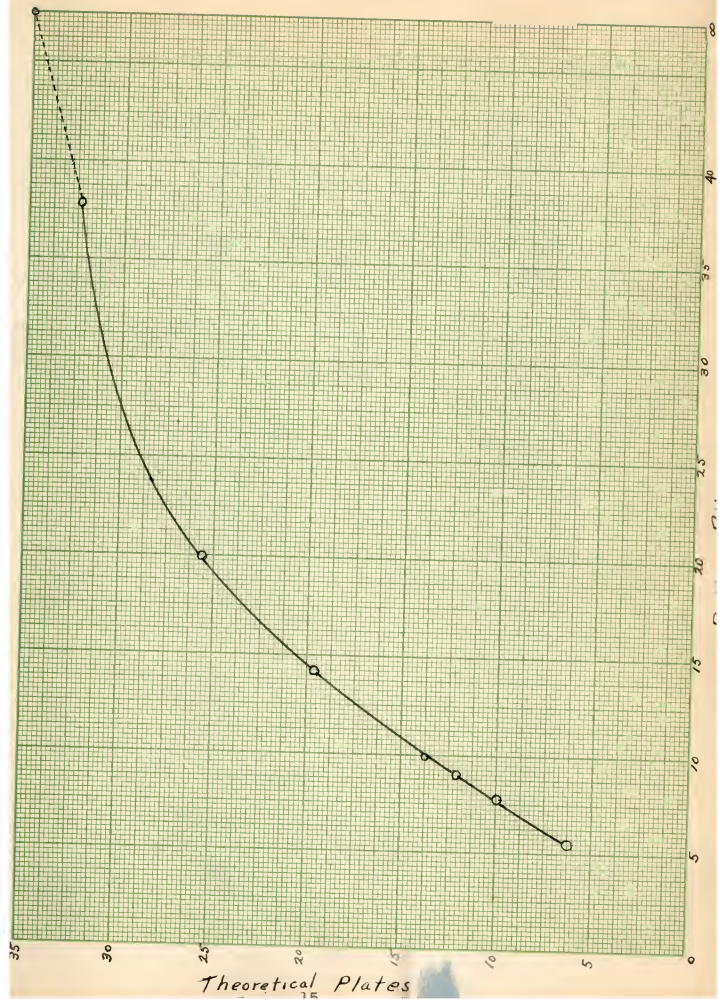
Data Obtained in the Determination of the Throughput Rate which gave minimum H.E.T.P. at Total Reflux and Atmospheric Pressure

Column No.	Throughput rate cc/hr	Head	Kettle	Total No. of Plates	H.E.T.P. in.
2	67	1.3918	1.4170	53	0.45
	90	1.3914	1.4174	55	0.44
	126	1.3904	1.4176	62	0.39
	270	1.3918	1.4162	50	0.48
	298	1.3912	1.4140	48	0.50
3	39	1.3956	1.4120	31	0.71
	40	1.3950	1.4115	31	0.71
	60	1.3933	1.4122	32	0.69
	72	1.3926	1.4106	35	0.63
	100	1.3940	1.4111	33	0.67

TABLE IV

Data to Determine H.E.T.P. at various Reflux Ratios and Atmospheric Pressure and at Optimum Throughput rate.

Column No.	Throughput rate cc/hr	Reflux Ratio	Head	Kettle	Total No. of Plates	H.E.T.P. in.
3	90	5 : 1	1.4048	1.4085	6	3.66
	81	9 : 1	1.4033	1.4109	12	1.82
	72	10 : 1	1.4020	1.4106	14	1.57
	81	14 : 1	1.3990	1.4118	20	1.10
	81	20 : 1	1.4028	1.4162	26	0.92
	81	38 : 1	1.3942	1.4115	32	0.67
	81	Total	1.3926	1.4106	35	0.63



Analytical Columns
(Twisted Stainless Steel Wire)

In the oxidations described in chapters II and III there were often obtained small amounts of material that could be separated best by fractional distillation but in such small amounts that it was not possible to separate them by any of the columns that have been described heretofore. It became apparent therefore that another type of packing must be used that would have much less holdup per theoretical plate to successfully separate these products.

Column No. 4 of the type reported by Bower and Cooke (8) was constructed of stainless steel in a manner described by them. It was found that if the packing were tight enough to fit all sides the force necessary to pull it into the tube was great enough to stretch the packing out of shape. The packing was made a bit smaller than they recommended and thus it was relatively easy to pull it into the tube when greased with oleic acid. The oleic acid was then removed with alcohol. The alcohol formed a continuous film between the packing and the tube, being broken about six times by the misfits in the packing. Standard taper joints were sealed to the tube and this was welded inside a heater jacket as shown in Fig. 3. The bulge at each end of the tube is to allow for expansion. This jacket was wound with

equally spaced nichrome wire so that about 300 watts would be obtained at 135 volts. This was enclosed inside an air jacket as in previous columns.

Since refractive indices and optical rotations are sometimes excellent guides for the separation of fractions, it was not feasible to use the Ellis type of receiver (14). In the use of this receiver, it is necessary to interrupt the distillation to obtain the fractions that have been collected. It was necessary to design a head with a small operating holdup that would permit the control of the reflux ratio and the collection of samples without interrupting the distillation. The head described in Fig. 4, page 21 was designed. By rotating the cold finger condenser the reflux ratio could be varied from 1 - 1 to about 30 - 1 with the stopcock open full. Further reductions in the reflux ratio could be controlled by partially closing the stopcock.

At total reflux the column was found to flood at about 300 cc per hour total throughput, instead of 180 cc per hour as stated by Bower and Cooke (8).

The results of testing this column are given in table V, page 22.

Since the packing must be drawn in with little force, a tight fit is impossible. It was necessary to heat the glass to the softening point so that the

glass tube would shrink to the packing. The column was placed in a quartz tube and the annular space filled with aluminum oxide. The latter compound is high melting and does not dissolve in the hot glass leaving the column transparent after the treatment. The quartz tube was heated by equally spaced nichrome wire and insulated with glass wool. It was found after the first experiment that no vacuum in the column was necessary and that it must be carefully heated. Since the column cannot be seen during the heating, the treatment was controlled by timing. After several experiments and slight redistribution of wire toward the ends of the quartz heating tube, a column was obtained that had just the tips of the wires imbedded in the glass and when finished produced a column whose characteristics are described in table VI.

It should be pointed out that care must be taken not to submit the column to either compressional or elongating forces while it is under the heat treatment. If the forces are compressional the tube bulges and the packing does not fit the tube. If the tube is elongated the packing is stretched and the tube collapses.

If the tube is heated too hot it completely collapses around the packing, or the packing sticks through the tube and forms small holes. These holes can be detected by means of a high frequency spark coil.

When the spark coil is held close to the tube the spark will jump directly to the hole instead of uniformly along the column. In either case the plate efficiency becomes very low and the column floods readily. The tube is weakened considerably and breaks easily.

Comparison of Packings

It will be seen by comparing tables I and VI that the twisted wire (column No. 5) has about the same H.E.T.P. as the small stainless steel spiral (column No. 3). The flood point in cc reflux per hour is only slightly lower in the case of the twisted wire and the holdup per theoretical plate is several times smaller, as seen by comparing tables II and VI.

Cost

The overall cost for the finished column with twisted wire screen packing is \$8.00 or \$4.00 per foot including accesories and labor figured at \$.1.50 an hour. The head described cost \$12.00 figuring labor at the same rate.

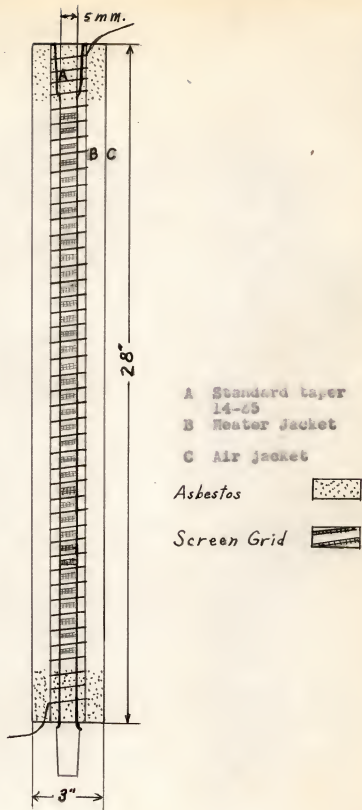
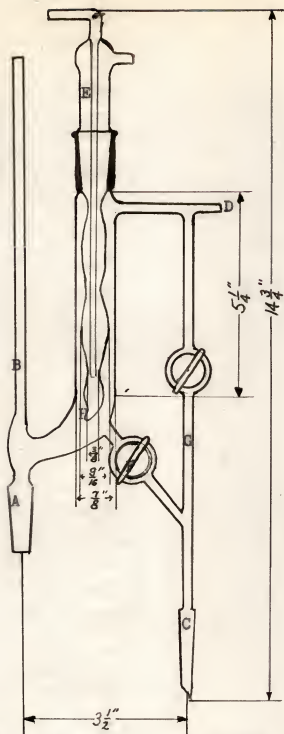


Fig. 3

Semimicro Distilling Column



A Standard taper 14-35

B Thermometer

C 11-28 standard taper

D Vacuum outlet

E Adjustable reflux ratio
cold finger condenser

F Stopcock (1 mm)

G 2 mm capillary

H Drip point, reflux
return

Fig 4 Semimicro Distilling Head

TABLE V

Data Obtained in Testing Column No. 4

Throughput rate cc/hr	Head	Kettle	Total No. of Plates	H.E.T.P. IN.
196	1.3937	1.4007	17	1.18
162	1.3919	1.4009	19	1.05
75	1.3921	1.4012	21	0.95
45	1.3918	1.4019	23	0.87
18	1.3924	1.4048	25	0.80

Throughput rate cc/hr	Pressure drop (at 20 mm)	Operating holdup	Operating holdup per plate
45	0.8 mm	0.8 cc	0.033 cc
162	1.0 mm	1.1 cc	0.057 cc

Non-drainable holdup is 0.4 g benzene

TABLE VI

Data Obtained in Testing Column No. 5 (Heat Treated)

Throughput rate cc/hr	Head	Kettle	Total No. of Plates	H.B.T.P. in.
18	1.3950	1.4120	32	0.69
45	1.3980	1.4135	30	0.73
82	1.3978	1.4140	29	0.76
180	1.3990	1.4142	26	0.92

Throughput rate cc/hr	Pressure drop (at 20 mm)	Operating holdup	Operating holdup per plate
18	1.0 mm	0.9 cc	0.028 cc
180	2.0 mm	1.2 cc	0.045 cc

Non-drainable holdup is 0.5 g benzene

Summary

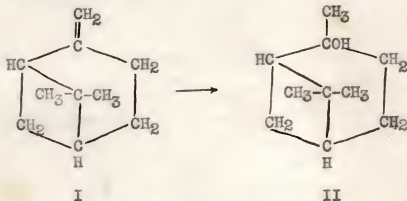
The efficiency of the stainless steel spiral is given. The theoretical plates and H.E.T.P. at various rates of throughput have been recorded. The operating efficiency of the spirals at different reflux ratios have been determined. The construction of a twisted spiral stainless steel column is described. The efficiencies of these columns are given. A new low holdup head has been designed.

Chapter II

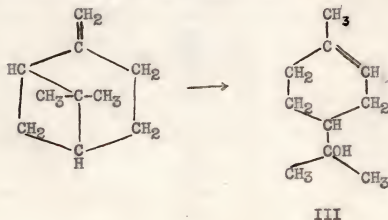
THE AIR OXIDATION OF BETA PINENE

Introduction

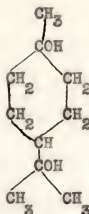
When β pinene reacts it may form several types of product. In some cases in the hydration of pinene, I, the ethylenic linkage is broken to form methylpininol, II (7).



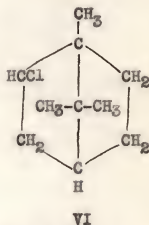
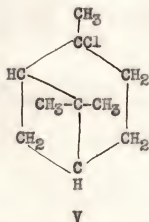
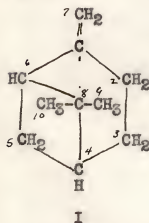
In other cases of hydration the cyclobutane ring is broken, forming α terpineol, III, (18).



Further hydration of either II or III yields 1-8 terpin, IV (59).

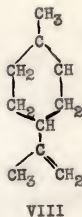
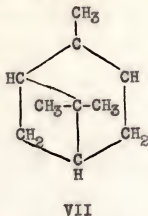
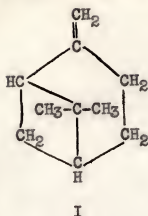


In some cases when there is an addition to the ethylenic linkage the reaction is accompanied by a Wagner-Meerwein rearrangement (52) to form derivatives of camphane. For example: when pinene is treated with dry hydrogen chloride at 0°, pinene hydrochloride, V, is formed which rearranges to camphene hydrochloride, VI (2).



Beta pinene polymerizes to a diterpene when heated under pressure (53). It isomerizes to α pinene, VII, (53) and to dipentene, VIII (44). This change does not

appear to be reversible (51).

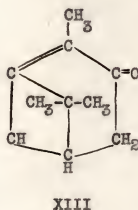
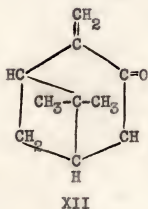
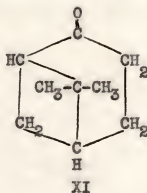
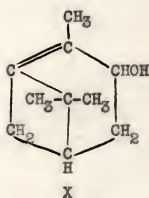
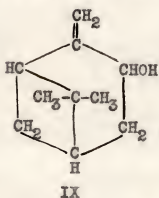


The molecule of β pinene, I, has two definite weak points for oxidizing agents; its ethylene linkage and the methylene group activated by the ethylenic linkage. This methylene group is in the 2 position.

Some oxidizing agents as permanganate (44), ozone (47) and nitric acid (4) attack the ethylenic linkage while others as selenium dioxide attack the methylene group (54) activated by the ethylenic linkage forming alpha unsaturated alcohols and ketones.

In this phase of the investigation, pinene was oxidized by air at different temperatures, with and without catalyst, and the oxidation products were identified as pinocarveol, IX, carvopineol, X, Nopinone, XI, pinocarvone, XII, and carvopinone XIII. Carvopinone and carvopineol are rather remarkable compounds in that their existence is contrary to the

Brendt rule (9) which states that a compound having an ethylenic linkage attached to a carbon atom that is apart of a dicyclic system is unstable and tends to isomerize to a more stable form. It should be mentioned, however, that these compounds are unstable and polymerize to a white solid upon standing.



Preparation of Beta Pinene

In all cases pinene was obtained by the fractionation of commercial material (24) through column No. 1, described in chapter I, at 20 mm pressure. The pressure was controlled by a sulfuric acid manostat of the Hershberg-Huntress type (29). The action of the pump on the manostat was direct and the column was connected to this system through a three gallon reservoir containing a small inlet and outlet so that the mercury in the Zimmereli gauge attached to the head of the column could be seen not to move. The gauge could be read to the nearest 0.1 mm of mercury. When this manometer was calibrated against a Germann (21) type of barometer, it was found that it would register the correct pressure within ± 0.2 mm.

The chief impurity in commercial α pinene is α pinene which boils about 8° lower at 20 mm. The material was collected at a reflux ratio of about 30 : 1 until the pure β pinene distilled. Then the reflux ratio was reduced to about 15 : 1. The distillate having constant physical properties was collected and used in subsequent oxidations.

The physical constants for all the β pinene used were b.p. 59.3° (20 mm), n_D^{25} 1.4768, d_4^{25} 0.8666 and

(a) $^{25}_D -21.4^\circ$. These constants are in close agreement with Palkin and coworkers (49, 41) and Stallcup, Fugitt and Hawkins (17A). Darmon (12) points out that pure α pinene has a constant specific rotation regardless of its source of -22.44° for Hg_2 light.

Beta pinene is rather rapidly attacked by air on standing (57). To verify this statement two portions of beta pinene of about 200 cc each were sealed in clear glass ampules. The ampules were flushed with CO_2 gas before sealing and one ampule set aside in the dark and the other in the open and allowed to stand for about six months. At the end of this time, the physical constants of the β pinene had not changed. No difference in the physical properties could be noticed after distillation through the semimicro column No. 3 described in chapter I.

Two other samples were kept in glass stoppered bottles and were examined after about three months. One bottle, which was filled so that there was scarcely more than two cc of air space showed no change in its physical constants while the other sample which only about half filled a glass stoppered bottle had a higher refractive index, a greater density and a higher optical rotation. It was not subjected to distillation.

Air-Oxidation Experiments

At room temperature- Air dried by calcium chloride was bubbled from a glass tube 4 mm i.d. at a rate of about 34 liters per hour through β -pinene at room temperature (20° - 28°) for sixty days. The products were identified as pinocarveol, carvopineol, pinocarvone, and carvopinone. A small amount of nopinone was detected. Polymerisation occurred in excess of 70% of reacted β -pinene. The polymer was pyrolyzed, and molecular weights and combustions were run. No acids ketones, nor alcohol derivatives could be formed. For complete data see table VII, 49

Silver catalyst at elevated temperature.- The silver catalyst was prepared by plating silver onto a silver foil 5 x 15 cm from a 1.0 molar silver nitrate bath for 30 minutes at 6 volts. The foil was rinsed and then baked at 140° for two hours. This method of preparation produces finely divided silver that readily flakes off the foil (31).

The foil was cut into strips about 2 mm wide and placed in the beta pinene which was maintained at 100 $\pm$.3° in a thermostat whose temperature was controlled by a Hershberg-Huntress (29) thermoregulator. The entering air was dried by calcium chloride and bubbled

from a glass tube 1 mm i.d. at a rate of about 40 liters per hour. The exit air passed through an ice-water cooled reflux condenser and an ice trap at temperatures below -20° . It was hoped to follow the reaction rate by the change in the refractive index and optical rotation of the mixture. However, after a short time the solution was so colored that the rotation could not be observed. Polymerisation was in excess of 60% of β -pinene reacted. Nopinone, pinocarvone, carvopinone were isolated and pinocarveol was detected. Several cc of water had collected in the ice trap and this gave an aldehyde test. No aldehyde could be separated and the positive test was possibly caused by a trace of formaldehyde as a byproduct in the oxidation of the pinene to nopinone. These data are listed in table VII, P.49

Ceric oxide catalyst.— Air was bubbled through pinene containing 0.2% ceric oxide at 100 . The apparatus was the same as described above and the experiments were carried out under the same conditions. Polymerization occurred to the extent of about 80% of the reacted β -pinene. Pinocarvone and carvopinone were isolated. The results are given in table VII.

Manganous Acetate Catalyst.— Air was bubbled through β -pinene containing 0.2% manganous acetate, using the same apparatus at a temperature of 85°. 70% of the reacted β -pinene polymerised. Pinocarvone and carvopinone were isolated. See table VII, P. 49

Cobalt Acetate in Acetic Acid.—0.2% Cobalt acetate was added to equal volumes of acetic acid and beta pinene and air bubbled through at 85°, using the same apparatus. A small amount of sodium acetate was added in the hope that any alcohol that formed would be esterified by the acetic acid. It has been found that anhydrous sodium acetate is necessary for the esterification of the secondary and tertiary pinene alcohols (54). Polymerisation occurred to the extent of 30% of the reacted β -pinene. Pinocarvone, carvopinone and pinocarveol, largely as its acetate, were isolated. A small amount of a high boiling acetate, probably contained some carvopinyl acetate, was fractionated out, for when this acetate was hydrolyzed, a compound was obtained by fractionation which had properties of the substance which was later identified as carvopineol (see page 41). Complete data are given in table VII.

Separation of the Oxidation Mixture

The reaction mixture was poured into a flask having a thermometer well, and the unreacted hydrocarbons were fractionated out. The column used was either No. 3 or No. 4 as described in chapter I, and the pot temperature was not allowed to exceed 78°. The hydrocarbons recovered by fractionation at 20 mm pressure included small amounts of α pinene, β pinene and in some cases small amounts of dipentene.

The remaining oils were steam distilled until the distillate was clear.

After the distillation the polymer was usually a sticky solid and was scraped from the flask. Water was removed from it by warming in a high vacuum.

The steam volatile oil was treated with either ethyl borate or boric anhydride (4%) and refluxed on the steam bath for two hours. At the end of this time the pressure was decreased and the temperature was increased until all the neutral oils were distilled over. The neutral oils were collected in a series of traps cooled to - 25°. The borate ester remaining behind was treated with sodium carbonate and steam distilled. The distillate was extracted twice with ether and the ether evaporated leaving the alcohols. The

alcohols were separated by fractionation through column No. 4.

The neutral oils were treated with about twice their volume of sodium bisulfite according to Schmidt (45). The strength of the bisulfite solution was 335 grams of sodium bisulfite and 105 grams of sodium bicarbonate in 1000 grams of water. The solution was shaken at intervals for two days for it has been shown that in some cases the bisulfite additions require an induction period of as much as a day or two (48). The mixture was extracted twice with ether. The bisulfite solution was treated with sodium carbonate and steam distilled with the intermitten addition of sodium carbonate until the runnings were clear. The ether extract of the distillate gave pinocarvone. To the aqueous portion was added 10 cc of 6 N. NaOH (57) and the steam distillation was continued until the distillate was clear after further additions of NaOH. The ether extract of this distillate was carvopinone.

The ether extract of the bisulfite solution in several cases gave small amounts of nopinone, along with very small amounts of the alcohols and ketones not removed by the previous treatment.

This procedure may be altered by treating the oil with bisulfite before it was treated with the boric anhydride. Since carvopinone polymerizes so

easily upon heating, it should be possible to isolate more carvopinone from the mixture by treating the oil with the bisulfite before it is treated with the boric anhydride.

There appeared to be a great loss in the bisulfite purification of carvopinone, so 10 g of pure carvopinone were treated with neutral bisulfite for two days and the resulting addition product steam distilled from sodium carbonate. An ether extract left nothing upon evaporation. The steam distillation was continued using sodium hydroxide as described above. The mixture which distilled was ether extracted and upon evaporation of the ether only 5.5 g of carvopinone remained. Most of the loss of carvopinone is due to polymerisation. Apparently none was isomerised to pinocarvone. Other experiments were not carried out, but the yield of carvopinone seems to depend on the time required and the temperature at which the bisulfite extraction is made. In all cases the yield does not exceed 60-70%.

Identification of Products

The hydrocarbon portion was fractionated and the dipentene readily separated. Most of the α -pinene and β -pinene were obtained by further fractionation. The cut intermediate between these two was considered to be made up only of α -pinene and β -pinene and analyzed by the application of Biot's rule (54). No other hydrocarbons with properties in this range could be found. Biot's rule is;

$$x = \frac{(a)_0 - (a)_2}{(a)_1 - (a)_2}$$

where

x is the mole fraction of the compound in question

$(a)_0$ is the specific rotation of the mixture

$(a)_1$ is the specific rotation of the pure compound in question

$(a)_2$ is the specific rotation of the other pure compound

The alpha pinene recovered had the following constants, b.p. (20 mm) $51^\circ - 52^\circ$, n_D^{25} 1.4636. The accepted values of Fugitt Stallcup and Hawkins(56) are b.p. (20 mm) 51.6° , n_D^{25} 1.4631, d_4^{25} 0.8542.

The β -pinene had the following constants, b.p. 59.2° (20 mm) n_D^{25} 1.4768 d_4^{25} 0.8665, which check with the values given on page 29.

Dipentene had the constants b.p. $72-73^\circ$ (20 mm) n_D^{25} 1.4705, d_4^{25} 0.8391. Fugitt (7) observed the

Values b.p. 52° (10 mm), n_D^{25} 1.4702, d_4^{25} 0.8387
(a) n_D^{25} -4.60° . A tetra bromide was also made by adding slowly 6 cc of bromine to 7 g of dipentene dissolved in 50 cc of glacial acetic acid. The crystals which formed after two days were filtered and dried. After recrystallization from methyl alcohol the crystals were dried on a clay plate. They melted at 124° - 125.5° . Wallach (63) reported 125° . Goldblatt and Palkin (25) reported 124.5° - 125.5° .

Neutral Oils

Pinocarveol: When purified through the borate ester and fractionated this compound had the following constants, b.p. 78° - 80° (3-4 mm), b.p. 86° - 87° (9 mm) b.p. 100° - 101° (20 mm) b.p. 209° (760 mm) n_D^{25} 1.4980 (a) n_D^{25} 65.5° d_4^{25} 0.977 M_D Calc (22) 45.52 found 45.72. Stallcup and Hawkins (55) report the following values for pinocarveol b.p. 78° - 80° (3-4 mm) n_D^{25} 1.4980 (a) n_D^{25} 65.5° 0.976. This pinocarveol solidified at about 5° . Schmidt reported a thaw point of 7° for pinocarveol purified through the phenylurethane (46).

Pinocarveol phenylurethane was prepared according to Schmidt (46). Equivalents of the pinocarveol and phenyl isocyanate were mixed and allowed to stand for two days. The crystals of the urethane were removed by suction and recrystallized from petroleum ether. The melting point was 86° - 89° . Palkin and Joshel report

84- 86° (42). Schmidt (48) reported 88-90°. Stallcup and Hawkins reported 88-89° (55).

Pinocarvyl acetate, when prepared in the manner described above and fractionated had the following constants b.p. 89-90° (3 mm), b.p. 225° (760), n_D^{25} 1.4762, d_4^{25} 0.994, $(\alpha)_D^{25}$ - 20°. Saponification number, calculated 194.26, found 193 or 99.4%. Schmidt reported b.p. 227-8, d_4^{20} 0.997, $(\alpha)_D^{25}$ + 15.8° for the d-isomer (48). Stallcup and Hawkins (55) reported b.p. 88-90° (2-3 mm), n_D^{25} 1.4750, d_4^{25} 0.991, $(\alpha)_D^{25}$ - 38°.

Pinocarvone- When purified through the bisulfite it had the following constants, b.p. 75-78° (3 mm), b.p. 88-89° (8 mm), b.p. 222-223° (760 mm), d_4^{25} 0.988, $(\alpha)_D^{25}$ - 16°, n_D^{25} 1.5019. M_D calculated 44.83, found 44.86. Schmidt (48) gives the following constants, b.p. 222-223° (760 mm), d_4^{20} 0.9881, n_D^{20} 1.50373, (α) + 13 to - 15°. Stallcup and Hawkins (54) reported b.p. 75-78° (3 mm), d_4^{30} 0.980, $(\alpha)_D^{30}$ - 16.5°, n_D^{30} 1.5000.

Pinocarvonoxime- This compound was prepared by the method of Beckman (6). One gram of the hydroxylamine hydrochloride was dissolved in 5 cc of water. Sodium bicarbonate was then added until evolution of carbon dioxide ceased. This solution was then shaken with one gram of carvopinone in three cc methanol. After standing for two days the oxime was removed by filtration.

On recrystallization from dilute ethanol, fine needles were obtained which melted at 68-68.5°(Corr.). Schmidt (48) reported 68-69°. Stallcup and Hawkins reported 68-68.5° (54).

Pinocarvone Semicarbazone- A saturated aqueous solution of semicarbazide hydrochloride and sodium acetate was prepared. 10 cc of this solution was added to a solution of pinocarvone in methyl alcohol. The semicarbazone precipitated almost immediately and the needles after recrystallization from dilute methyl alcohol melted at 212-213° (corr.). Schmidt (48), reported 212-215°. Stallcup and Hawkins reported 212-213° (54).

Pinocarvone 2,4-Dinitrophenylhydrazone- 2 grams of pinocarvone were added to 100 cc of an alcoholic solution of 2 grams of 2,4-dinitrophenylhydrazine (50) and the solution brought to boil. 2 cc of concentrated HCl were added. The 2,4-dinitrophenylhydrazone formed immediately. After boiling for three minutes the crystals were filtered out, dried and recrystallized from ethanol. They melted at 222-223° (corr.). Stallcup and Hawkins reported 223-223.5° (54).

Carvopinone- This compound has the following constants when purified through the bisulfite addition product, b.p. 82-84° (3 mm), d^{25}_4 0.980, $(\alpha)^{25}_D$ 62.0°, n^{25}_D 1.4935. M_D calculated 44.83 (22) found 44.70.

Stallcup and Hawkins reported 82-84° (3 mm), d^{20}_4 0.973, $(a)^{20}_D$ 62.7°, n^{20}_D 1.4910. Wallach and Englebrecht (65) reported an oil with a b.p. 95-96° (12 mm).

When carvopinone is exposed to the air at room temperature, it slowly turns yellow and forms a white solid polymer insoluble in the common solvents. When carvopinone is freshly distilled and sealed under CO₂ gas it seems to keep much better but gradually polymerizes.

Carvopinoxime- This compound was prepared by the method of Beckman (6) and after recrystallization from aqueous methanol melted at 131-133° (Corr.). Wallach (64) reported 132°. Stallcup and Hawkins reported 131-133° (54).

Carvopinone Semicarbazone- This compound was prepared by the method of Schmidt (48). This required two or more days for the semicarbazone to form. After recrystallization from aqueous methanol the crystals did not melt below 300° as recorded by Wallach and Englebrecht (65).

Carvopineol- When this compound was separated from the borate ester it had the following constants, b.p. 95° (3 mm), b.p. 112° (20 mm), $(a)^{25}_D$ - 31.5°, n^{25}_D 1.4959, d^{25}_4 0.972. Analytical; Carbon found 78.51 calculated 78.89, Hydrogen found 10.49, calculated 10.59. Carvopineol is C₁₀H₁₆O.

Carvopinyl Phenylurethane: This was prepared by mixing equivalents of the alcohol with phenylisocyanate. The alcohol dehydrates very easily for the first attempts gave the phenyl isocyanates' hydration product, diphenyl urea. After several attempts a urethane was obtained that melted at 78-80° after recrystallization from heptane (b.p. 90-100). Further recrystallizations did not change its melting point. Analytical for $C_{17}H_{21}O_2N$. Carbon found 74.9, calculated 75.4. Hydrogen found 7.84, calculated 8.01. Attempts to form the α naphthylurethane, 3,5 dinitrobenzoate and the 3 nitrophthalate failed.

Hopinone: This compound when fractionated from the remaining neutral oils had the constants b.p. 80-82° (8 mm), d^{25}_4 0.980, n^{25}_D 1.4802, $(\alpha)^{25}_D$ 16.7°. Ousling (39) found b.p. 209°, d^{20}_4 0.981 $n^{20.5}_D$ 1.4787 (α) 18.46°, with a melting point somewhat above 0°. This oil did not solidify at -10° and probably contained a small amount of pinocarpone, tho the amount of this impurity was small since these constants are close to those of Ousling.

Hopinone Semicarbazone: 6 grams of semicarbazide hydrochloride and 9 g of sodium acetate were dissolved in 20 cc of water. 1 cc of the ketone in 10 cc of

methanol was added and allowed to stand for two days. The crystals were removed by filtration and when recrystallized twice from aqueous methanol melted at 186-187°. Bayer and Villiger who first reported the semicarbazone reported a m.p. of 180°.

Analysis of the polymer: In all cases the extent of polymerization is high in the air oxidation of beta pinene. Molecular weight determinations gave results of 850 to 1050. The greater the temperature and time of oxidation the higher was the molecular weight.

When this polymer is destructively distilled at atmospheric pressure, in the presence of air, a "Pine Oil" is obtained. Its boiling range is 225° to 375° with no definite fractions. The first fractions are light straw color and the end fractions are darker brown or red in color. From about 40 grams of polymer 26 grams of oil was obtained. When this 26 grams of oil was fractionated through column No. 4, described in Chapter 1, at 10 mm pressure the following fractions were obtained.

Fraction	Weight	b.p. (10 mm)	n_{D}^{25}
1 1	1.0 g	62-75°	1.4640
2	2.0	76-86°	1.4600
3	3.0	86-101°	1.4568
4.	1.5	101-111°	1.4551
5.	1.7	111-121°	1.4584

Fraction	Weight	b.p. (10 mm)	n_D^{25}
6	1.6 g	121-130°	1.5022
7	2.7	139-151°	1.5030
8	3.0	151-180°	1.5180
9	2.0	180-200°	1.5210
10	6.0 (residue)		

Attempts to form alcohol derivatives and ketone derivatives were not successful. No acids could be detected. It is true however, that no derivatives of the terpene alcohols or ketones will precipitate if they are not pure (54).

Data on the combustion of fraction 3 gave C 71.9% and H 8.1%. The combustion of fraction 8 gave C 84.4%, H 4.3%. These results show that oxygen is a constituent of the polymer.

Samples of polymer of 30 g each were sealed in glass tubes and heated in autoclaves for different lengths of time and at various temperatures from 275° for six hours to 350° for 72 hours. The sample heated for 6 hours at 275° gave 25 cc of a gas that burns with a characteristic hydrogen flame and 6 cc of water and a harder polymer, which upon destructive distillation at atmospheric pressure gave about 50% yield of an oil with the boiling range 275-375°. n_D^{25} 1.5073, d_4^{25} 1.013, Viscosity .201 poise, Surface tension 30 dynes/cm. Other tubes were similar. The tube heated to 350° for 72 hours gave 10 cc water,

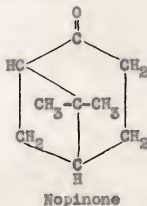
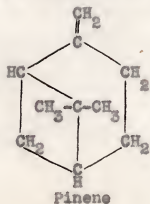
45 cc gas, mostly hydrogen, and a charred polymer, which upon destructive distillation gave little oil under 375°. Attempts to heat the polymer higher or longer caused the pyrex tubes to explode.

Destructive distillation of the polymer at atmospheric pressure gave an oil with the boiling range of 250-375°, n_D^{25} 1.4980, d_4^{25} 0.991, Viscosity at 30° 0.191 poise, surface tension at 30° 32 dynes/cm.

The polymer was destructively distilled in a high vacuum (2 mm). The oil had a boiling range of 200-375° at atmospheric pressure. The yield was greater, being about 75% of the polymer. n_D^{25} 1.4923, d_4^{25} 0.986, Viscosity³⁰ 0.186 poise, surface tension³⁰ 31 dynes/cm.

Discussion

The methylene group, in the position 2 of the molecule of pinene is activated by the ethylenic linkage. This methylene group is attacked by air, with and without catalyst, to form unsaturated alcohols and ketones. At the lower temperatures the ethylenic linkage was attacked to form nopinone.



The formation of the newly described carvopineol led to the speculation as to whether it was an intermediate in the oxidation of beta pinene to carvopinone. Some light could be thrown on this question by oxidizing carvopineol with an oxidizing agent that does not attack ethylenic linkages. It has been shown that selenium dioxide generally attacks a methylene group, or methyl group, activated by an ethylenic linkage (54). Hence the following experiment was carried out. 2 grams of carvopineol was treated with 0.5 g of pure selenium dioxide in 10 cc ethanol and refluxed for two hours. The mixture was steam distilled and treated with bisulfite solution. Ether extraction of the bisulfite solution gave only ethanol. When the bisulfite was made alkaline with sodium carbonate, followed by steam distillation, no oil was detectable. The addition of sodium hydroxide, followed by steam distillation, gave an oil with the odor of carvopinone. Ether extraction gave less than 0.3 gram of oil. It was identified as carvopinone by its oxime. The constants closely checked those previously given.

14 g of pinocarveol were dissolved in 75 cc ethanol in a flask equipped with a mechanical stirrer and reflux condenser. 5 g of selenium dioxide were slowly added and refluxed three hours. The mixture was steam distilled and gave 8 grams of oil. The

oil was treated with neutral bisulfite and ether extracted. No oils were obtained. The bisulfite gave 0.4 g of pinocarvone and 3 g of carvopinone.

Obviously, carvopineol is not necessarily an intermediate in the formation of carvopinone. However the ability to oxidize the described carvopineol to carvopinone is offered as evidence of the structure of the alcohol.

Both carvopinone and pinocarvone are unstable and polymerize at room temperature. The rate is greatly accelerated at higher temperatures. When beta pinene is oxidized in an esterifying medium the pinocarvyl acetate is the main product and there is a sharp decrease in the amount of polymer. Since both pinocarvone and carvopinone were identified in the esterified media, it seems that the polymerization occurs from these two substances. When this polymer is pyrolyzed, it disintegrates into a complex system of molecules. No fraction could be obtained as a pure compound and no derivatives of alcohols, aldehydes, ketones or acids could be formed.

Since the yield of polymer is high, efforts have been made to find a use for it or its thermal decomposition products. The boiling range, viscosity, density, surface tension, and other physical constants

are given in view of the fact that these constants are used to determine a compound's usefulness in flotation processes or as a plasticizer.

TABLE VII

Data on the Air Oxidation of Beta Pinene

Experiment No.	Weight Pinene	% Catalyst	Time	Temperature degrees C	% β -Pinene	% α -Pinene	% Dipentene
1	1504 g	--	60 days	20-28	20.5	6.3	--
2	136	Ag foil	24 hours	100	40.8	4.1	3.3
3	152	" "	72 "	100	21.6	4.4	3.2
4	161	" "	60	60	33.3	2.2	1.9
5	142	" "	60	60	35.2	2.0	1.9
6	152	CeO ₂ (0.2%)	48	100	23.0	1.1	--
7	150	Mn(Ac) ₂ (0.2%)	20	85	36.9	3.5	2.1
8	149	" "	60	85	18.0	3.0	2.4
9	100 in 100 g HAc	Co(Ac) ₂ (0.2%)	65	85	18.0	2.0	--
10	150 in 150 g HAc	" "	60	85	21.0	1.4	--

TABLE VII

Data on the Air Oxidation of Beta Pinene

Experiment No.	% Nopinone	% Pinocarveol	% Pinocarvone	% Carvopinone	% Carvopineol	% Polymer	% Recovery
1	1.1	3.6	2.0	0.9	0.3	56.6	91.3
2	2.1	--	2.4	2.5	--	30.0	85.8
3	1.6	--	5.7	4.8	--	49.8	91.1
4	3.6	5.0	6.4	3.5	--	34.2	89.9
5	3.9	4.8	5.8	4.2	--	35.4	93.2
6	--	--	3.8	1.5	--	65.6	95.0
7	--	3.2	3.5	trace	--	41.9	91.1
8	--	4.2	1.8	--	--	62.0	92.3
9	--	3.2 as alc. 36.0 as acetate	3.2	2.0	0.2 as acetate	20.2	84.8
10	--	2.2 as alc. 31.0 as acetate	2.4	2.6	0.4 as acetate	26.3	87.3

Summary

Beta pinene was oxidized with and without catalyst and the products were pinocarveol, pinocarvone, nopinone, carvopinone, and carvopineol. Carvopineol is a newly described compound. The yields of these were small and polymerization is excessive. The large decrease in polymerization when oxidation takes place in an esterifying medium seems to indicate that the polymerization is from the pinocarvone and the carvopinone formed. The polymer was destructively distilled and the product shown to be a complex mixture of oxygenated compounds. Physical constants are quoted on the oils obtained by this destructive distillation.

Chapter III

ELECTROLYTIC OXIDATION OF PINENE

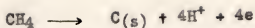
Introduction

A review of the literature showed that only two reference are given on the electrolytic oxidation of pinene or turpentine. Renard (45) oxidized turpentine at a lead dioxide anode and obtained p-cymene, an alcohol, b.p. 210-214°, a sulfonic acid $C_{12}H_{24}O_7S$, terpin hydrate and a resin. About sixty years later Fichter and Schetty (47) repeated the experiments using pinene b.p. 155-159°, (a) 34° in a dilute sulfuric acid emulsion with a lead dioxide anode and obtained p-cymene, dipentene, cineol, terpineol, terpin hydrate, terebic acid and a resin.

It seemed advisable to repeat these experiments using pure substances and recording other available physical constants, and in addition to determine just how much reaction was due to hydration and how much to oxidation.

In addition it should be possible to isolate different oxidation products when pinene is oxidized in different media and at different anodes.

Oxidation is the decrease of electrons in the atom, hence if at the anode



then the methane is oxidized. From free energy considerations the reversible potential would be - 0.13 volts when the hydrogen ion is at unit activity, as shown by theoretical considerations on page 64.

However when hydrocarbons are placed in a cell the resistance of the cell is so great that a conductor of electricity must be present. The only way so far devised is by the emulsion of the organic compound in water containing an electrolyte.

When a potential of less than that required to decompose water is applied to such an emulsion no appreciable current flows and if oxidation occurs it is at such a slow rate that no oxidation is observed in any reasonable length of time. Thus it appears that some form of oxide must be formed with an energy high enough to overcome the organic compound's reversible oxidation potential, and to supply its energy of activation.

Unfortunately little is known of the science of kinetics and of energies of activation. Actual reversible potentials of organic compounds would occur at an infinitely slow rate of reaction. In these experiments oxidation is observed only at potentials that are very

much greater than the theoretical values. In this study different anode potentials have been applied in different media containing the emulsified organic compound, and the products isolated and identified.

While it is realized that this is advancing an art rather than a science, a theoretical background is given so that empirical facts can be compared with the theoretical. The author hopes that at some future date the data here recorded may be used to help correlate empirical facts with reversible oxidation potentials of organic compounds and energies of activation. A thorough study of products formed at certain potentials in different media and different anodes should reveal catalytic effects that reduce energies of activation so that oxidation occurs at potentials that approach theoretically calculated ones.

Thus the purpose of these experiments are two-fold: (1) To critically reexamine previous experiments as to products formed and (2) to record as much physical data as possible concerning each experiment so that at some future date it may be of some help in correlating empirical facts and theoretical considerations.

Fundamentals of Electrolytic Processes

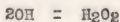
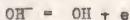
The passage of an electric current through an aqueous solution results, in general, in the liberation of oxygen at the positive electrode, or anode, and hydrogen at the negative electrode or cathode. Therefore, electricity can be regarded as an oxidizing or reducing agent under appropriate conditions. Although Faraday (15) contributed a large number of experimental observations to the subject of electrolytic oxidation and reduction of organic compounds, his work along this line was only empirical and it was Kolbe (18) who laid the foundation of the modern work on electrolytic oxidation and reduction. Kolbe stated that anodic oxygen is "One of the most valuable of oxidizing agents which is at the disposal of the chemist since its intensity may be varied, either by concentrating and heating the liquid or by increasing or diminishing the number of elements producing the electrical current."

Electricity makes available a clean and controllable method of bringing about oxidation and reduction, and even halogenation and the introduction of various groups into organic molecules. It is unnecessary to add special chemical reagents, from which the products

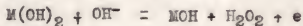
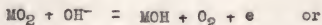
of the reaction must subsequently be separated, and the possibility of widely altering the nature of the process by varying the operating conditions, are advantages of the electrolytic method.

Mechanism of the Reaction

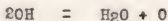
There are usually considered three mechanisms of anodic oxidation. Glasstone and Hickling (23) postulate the hydrogen peroxide theory.



Latimer (32) states the metallic peroxide theory is just as plausible.



Walker and Weiss (62) postulate the direct formation of molecular oxygen.



Probably no one mechanism can be given to include all types of electrodes and electrolytes.

Most organic anodic oxidations are not reversible and their reversible oxidation potentials cannot be measured.

Very little is known of the kinetics of these reactions or of their energies of activation. The general direction or the ability of a reaction to take place may be determined by solving for its reversible oxidation potential from free energy data.

$$W_{\max} = P V$$

$$W_{\max} = \int P dV$$

and for a perfect gas, $PV = RT$ for one mol.

so
$$W_{\max} = \int \frac{RT}{V} dV \quad \text{and for a perfect gas}$$

$$W_{\max} = \int \frac{RT}{P} dP \quad \text{and upon integrating}$$

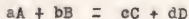
$$W_{\max} = RT \ln \frac{P_1}{P_2} \quad \text{for 1 mole of gas}$$

$$W_{\max} = nRT \ln \frac{P_1}{P_2} \quad \text{for any No. moles of gas}$$

and since partial pressures are analogous to concentration, and for an isothermal reaction

$$F = -nRT \ln \frac{a_1}{a_2} .$$

In any reversible reaction



and a_A , a_B , a_C , a_D correspond to the activity of the components A, B, C, and D in equilibrium at constant temperature

If the activity is changed to a' then there is a shift in the equilibrium and the change in free energy is given by

$$F_1 = aRT \ln \frac{a_A}{a'_A} \quad \text{where } a' \text{ is the new activity.}$$

Similarly:

$$F_2 = bRT \ln \frac{a_B}{a'_B}$$

$$F_3 = cRT \ln \frac{a_C}{a'_C}$$

$$F_4 = dRT \ln \frac{a_D}{a'_D}$$

or the change in free energy for the reaction is

$$F = F_1 + F_2 + F_3 + F_4$$

$$F = aRT \ln \frac{a_A}{a'_A} + bRT \ln \frac{a_B}{a'_B} + cRT \ln \frac{a'_C}{a_C} + dRT \ln \frac{a'_D}{a_D}$$

$$F = -RT \ln \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b} + RT \ln \frac{a'_C^c \times a'_D^d}{a'_A^a \times a'_B^b}$$

The last term represents any activity while the former represents the activity at equilibrium and is defined as the equilibrium constant, K_a . Then

$$F = -RT \ln K_a + RT \ln \frac{a'_C^c \times a'_D^d}{a'_A^a \times a'_B^b} \quad (1)$$

And from thermodynamic relations*

* The terms used here are those of Lewis and Randall "Thermodynamics and the Free Energy of Chemical Substances", McGraw Hill, 1923.

$$\Delta F = \Delta A + \Delta(PV) = \Delta E - \Delta(TS) + (PV)$$

From the first law $E = q - W = q - p\Delta V - W_e$

$$\Delta F = q - p\Delta V - W_e - \Delta(TS) + \Delta(PV)$$

Differentiating

$$dF = dq - PdV - W_e - TdS - SdT + PdV + VdP$$

and for a reversible process

$$dq = TdS$$

$$dF = -SdT + VdP - W_e$$

and at constant temperature and pressure

$$\Delta F - W_e \text{ but } W_e \text{ is defined as } nEF$$

$$\Delta F = -nEF \quad (2)$$

substituting equation 2 in equation 1

$$E = \frac{RT}{nF} \ln K_a - \frac{RT}{nF} \ln \frac{a'_C{}^c \times a'_D{}^d}{a'_A{}^a \times a'_B{}^b} \quad (3)$$

and when the reaction is so planned that the reactants start at unit activity and the final products are at unit activity then,

$$- \Delta F^0 = RT \ln K_a \quad \text{so}$$

$$E^0 = \frac{RT}{nF} \ln K_a \quad (4)$$

and substituting equation 4 into equation 3

$$E = E^0 - \frac{RT}{nF} \ln \frac{a'_C{}^c \times a'_D{}^d}{a'_A{}^a \times a'_B{}^b} \quad (5)$$

Where E° is the potential when the activities of the products and reactants are at unit activity.
 n is the No. of Faradays involved in the reaction as written.

F is one Faraday or 96,496 coulombs.

R is the gas constant

T is the temperature in degrees absolute.

It can be seen that if the free energy change is known, equation 2 can be used to calculate the theoretical oxidation potential. If the concentration of reactants and products is known at equilibrium, equation 5 can be used to calculate the potential. In most organic work the reactions are not reversible so the theoretical potentials are calculated from free energy data.

The free energy of the elements in the standard states is taken as zero. The standard state of the elements is taken as their most stable form at 25° and 1 atmosphere of pressure. The standard state of the hydrogen ion is taken at an activity of 1 molal. For the succeeding calculations, all acid solutions are considered as 1 molal and basic solutions as 1 molal.

The free energy data for inorganic compounds are from Latimer (32). The free energy data for

Organic compounds are from Parks and Huffman (43).

From the free energy of atomic oxygen (55025 cal) and the free energy of water (-56,690 cal) one calculates for the oxidation of water to atomic oxygen

$$\text{H}_2\text{O}(l) = \text{O}(g) + 2\text{H}^+ + 2e$$
$$E^0 = - \frac{F}{nF} = - \frac{(111,715)}{(2)(23066)} = - 2.42 \text{ volts}$$

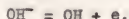
The high negative value for the potential indicates the difficulty in the oxidation of water with the formation of atomic oxygen as an intermediate step.

From free energy data, one calculates for the water-hydrogen peroxide couple in acid solution

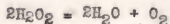
$$2\text{H}_2\text{O}(l) = \text{H}_2\text{O}_2(aq) + 2\text{H}^+ + 2e$$
$$E^0 = - \frac{81,910}{(2)(23066)} = - 1.77 \text{ Volts}$$

since the free energy of $\text{H}_2\text{O}_2(aq)$ is - 31,470 cal. (43).

Latimer (32) states that the assumption is frequently made that the first and rate determining reaction is

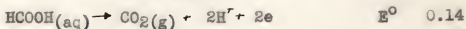
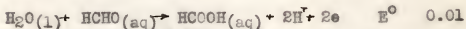
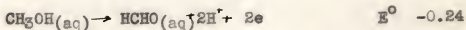
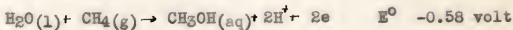


If this is the case because of its lower oxidation potential, hydrogen peroxide would be formed, and the oxygen then formed by the catalytic decomposition of hydrogen peroxide.

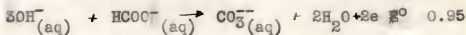
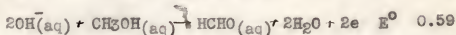
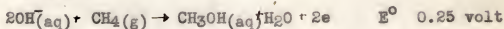


Even the reversible equilibria cannot be attained at room temperature for most organic compounds, the potentials for the various steps in the oxidation of

the hydrocarbons are of considerable interest. These potentials are worked out from the free energy data of Parks and Huffman (43). In the oxidation of methane the following reactions take place in a 1 M acid solution.



While the following represent the reaction in a 1 M basic solution.



The E° 's have been calculated from the following free energy data of Parks and Huffman (43) and the equation

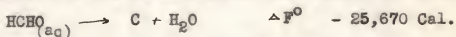
$$E^\circ = - \frac{\Delta F}{nF}$$

Material	F (at 25°)
$\text{CH}_4(\text{g})$	-12,200
$\text{CH}_3\text{OH}(\text{aq})$	-42,110
$\text{HCHO}(\text{aq})$	-31,020
$\text{CO}_2(\text{g})$	-94,450
$\text{HCOOH}(\text{aq})$	-88,110
$\text{CO}_3^{2-}(\text{aq})$	-126,390
$\text{HCOO}^-(\text{aq})$	-83,000
$\text{H}_2\text{O}(\text{l})$	-56,690
$\text{H} (1 \text{ M})$	0
$\text{OH}^-(\text{aq})$	-37,585

A number of important free energy relations should be noted. Formaldehyde is unstable with respect to the formation of glucose

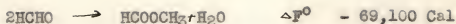


This reaction appears to be a step in the synthesis of cellulose in plants. Formaldehyde is also unstable with respect to its decomposition into carbon and water



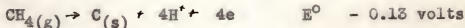
but there appears no evidence that this reaction occurs.

From free energy consideration, formaldehyde should oxidize and reduce itself.



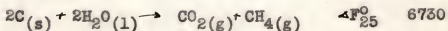
Experimentally this reaction goes slowly with the formation of methyl formate.

It must be noted in comparing thermodynamic predictions with actual experiments, the thermodynamics only states the possibility of the reaction, and not how rapidly it may take place. Unfortunately the unknown factors of kinetics and energy of activation are often the controlling factors in these reactions. For example: Judging merely from the free energies, one would conclude that carbon was a fairly good oxidizing agent.



However in view of the high energy of the C-C bond in solids it is not suprising that the activation energy is so large that even at high over voltages, carbon cannot be reduced to methane. Over voltage is defined as the difference in potential of an electrode at which a gas is being evolved by electrolysis at a definite current density and the reversible potential in the same electrolyte.

Thermodynamically carbon is stable with respect to hydrolysis



This postive free energy is not large, and except for

the activation energy, appreciable partial pressures of the gaseous products would be obtained, as shown by the equation

$$-\Delta F^0 = RT \ln K_p$$

and since the pressure of water and solid carbon at 25° is constant K_p becomes

$$K_p = p^{CO_2} \times p^{CH_4}$$

$$- 6730 = (1.99)(298) \ln(p^{CO_2} \times p^{CH_4})$$

so the pressure of CO_2 and CH_4 at equilibrium would be about 3 mm each.

Actually this reaction does go at much higher temperatures.

Other Influencing Factors on Electrolytic Oxidation

Temperature- Observations have shown that a rise in temperature decreases the over voltage of the cell, and causes the reaction to proceed more rapidly. However oxidation takes place more easily the higher the overvoltage, and hence the effect of raising the temperature cannot be generalized.

Anodic Material- The composition of the anode affects the over voltage, tho sometimes its effect is also catalytic. The catalytic affect of the

electrode material may in some cases completely outweigh considerations of potential. Thus, in the formation of periodate by the electrolysis of iodate in an alkaline solution with a smooth platinum anode, the potential rises during electrolysis and the yield correspondingly increases, and thus it appears that the potential is the governing factor in the oxidation process. With a lead dioxide anode however, the yield is greatly improved although the potential is lower than with a platinum electrode (37). In electrolytic oxidation of methyl alcohol in a dilute sulfuric acid solution it has been found that at a smooth platinum anode formaldehyde was obtained with a yield of about 80%, but at platinised and lead dioxide anodes the formaldehyde yields were only 40% and 15% respectively. This can be explained as due to oxidation to formic acid and carbon dioxide which takes place in spite of the lower over-voltages (13).

Temperature of Anode Due to Local Heating-

A phenomenon, probably of great importance, to which little attention has been given, is that the anode in electrolytic oxidation processes is probably at a high temperature, because of the great heat given out by the oxidation reactions and by the expenditure of energy in overcoming polarization resistances.

By the use of tubular electrodes containing thermometers, or by means of thermocouples embedded in the electrode surfaces it has been shown that there is a marked rise of temperature on electrolysis, especially with anodes at which oxygen is being produced (35). Fichter (16) has shown numerous cases of reactions which apparently occur at ordinary temperatures during electrolysis but which require a high temperature when carried out chemically. Kaufler (26) has shown that by heating an electrode with a subsidiary current its activity can be increased; thus with a heated platinum anode p-nitrotoluene was oxidized to p-nitrobenzoic acid instead of the p-nitrobenzyl alcohol usually obtained.

Influence of Current Density- When the products of electrolysis are unstable and it is desired to attain as large a yield as possible with the minimum of decomposition, a high current density is advantageous. This has been shown by Muller and Schellhass (38). In the present work the greater the current density the greater the anode potential was, provided other factors remained the same. See table VIII.

Nature of the Electrolyte- The potential of an anode at which oxygen is being formed is less in an alkaline than in an acid solution at the same current density. Thus the same current flows at a lower potential

and hence it appears that electrolytic oxidation might be less intense in an alkaline electrolyte. This was found to be the case in this work in that products were obtained in alkaline medium which did not appear when an acid medium was used as these compounds were further oxidized to end products.

Oxygen Carriers- Electrolytic oxidation processes are frequently aided, and sometimes the nature of the product is changed, by the addition of a catalyst or oxygen carrier. These are generally inorganic ions capable of undergoing reversible oxidation and reduction. No oxygen carriers were added in these experiments.

Experimental

The following experiments are described in a chronological order rather than according to facts found. The correlation of facts is given in the summary.

Equipment- The direct current was supplied by a motor-generator set capable of producing up to 20 volts and a current up to 20 amperes. The voltage was controlled by means of a rheostat connected in the field of the generator.

The cell was an unglazed Coors clay cup (76 mm x 150 mm) of about 600 cc capacity. The anode was placed inside the cup.

The platinum anode consisted of two pieces of gauze 5 cm x 8 cm each.

The lead dioxide anode was made by electrolyzing a lead electrode at the anode in a dilute sulfuric acid solution until it was completely coated with lead dioxide. It had a total surface area of 240 sq. cm. (20 x 6 cm).

The cathode in all cases was a copper sheet having a total surface area of 450 sq. cm.

The cathode compartment was a 4 l beaker and contained in addition to the catholite, a stirrer, the cathode, a heater and a thermoregulator sensitive to about $\pm 0.3^{\circ}$. This was placed in a 5 gal. pyrex jar containing water which was cooled by circulating ice water through a Ni-Cu coil.

The clay cup contained in addition to the anode, the anolyte, a variable mechanical stirrer, and a calibrated thermometer that could be read to the nearest 0.1° . An opening was provided in the head as an air inlet so that the vapors could be sucked through an ice trap whose temperature was below -20° . This minimized evaporation losses.

The current passing through the cell was registered by an ammeter which could be read to about 2%.

The cell voltage was determined by a voltmeter connected across the anode and the cathode and could be read to the nearest 0.1 volt.

The anode potential was measured by dipping an agar agar bridge saturated with KCl into the anolyte and connecting it to a calomel half cell. The liquid junction potential was neglected. The other half of the cell was connected through a student potentiometer to the anode; thus the potential between the anode and the anolyte could be measured to the nearest 0.001 volt. When the electrode potential was measured between the bottom of the anolyte and the anode, it was found to vary considerably from the potential measured between the top of the anolyte and the anode. The variation was often as much as 100%. The rate of stirring had little or no effect on this difference in potential. The only explanation of this phenomenon suggested is that there are charged gases rising to the top of the solution causing a higher concentration of positive charge at the top of the solution.

The potential at corresponding levels from the anolyte to the anode was measured and then the potential from the anolyte to the cathode was measured and the

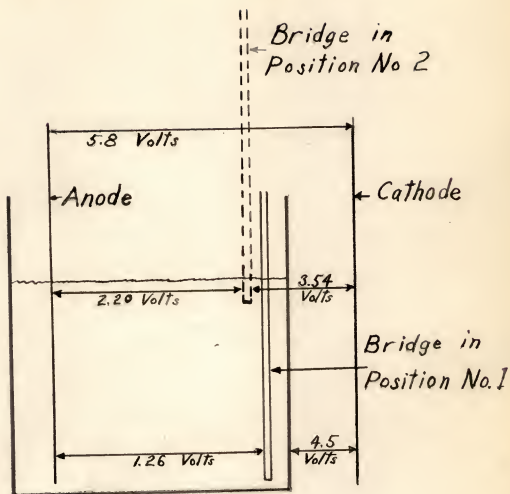


Fig. 5 Anode Potentials

sum of the potentials as shown in Fig. 5 was always equal to the potential measured from the cathode to the anode by the voltmeter within experimental error of reading of the instruments. For example in one reading: The potential across the cell was 5.8 volts. The potential from the bottom of the anolyte to the anode was 1.26 volts and the potential from the bottom of the anolyte to the cathode was 4.50 volts or a total of 5.76 volts. And similarly from the top of the anolyte to the anode was 2.20 volts and the potential from the top of the anolyte to the cathode was 3.54 volts or a total of 5.74 volts. Since the voltmeter could be read to only 0.1 volt these readings are well within experimental error. The electrode potential as shown in table VIII was read from the bottom of the anolyte to the anode.

Conditions of the Experiment

The first set of experiments consisted of two electrolytic oxidations using 85% alpha pinene (chief impurities were camphene and β pinene) at platinum anodes and with acetic acid-water solutions. No acids were formed and the only oxidation products was a mixture of tri- and tetraacetates. These were determined by saponification equivalent by the use of standardized KOH in ethylene glycol. These were difficult to hydrolyze and no alcohols could be identified

upon hydrolysis. Terpineol and terpin hydrate were identified as hydration products. Terpineol was identified as its phenylurethane and the terpin hydrate was identified by its mixed melting point of 112-113°.

Two experiments using lead dioxide anode and 85% pinene (table VIII) under conditions similar to those of Fichter and Schetty (17) were carried out. The products were similar to those obtained by them but no p-cymene or cineol were found. Chadwick and Palkin (18) have shown that both p-cymene and cineol are natural products of crude turpentine. Since few constants are quoted on the turpentine used by Fichter and Schetty, it is likely that these compounds were already in their turpentine

The next series of two experiments (table VIII) was made starting with pure pinene using 10% sulfuric acid as the anolyte with a platinum anode. Pinene, pinene, polymer, and hydration products of terpin hydrate and terpineol were obtained. When pinene was stirred in the presence of sulfuric acid and no current passed through it, the products were the same except the total recovery was greater and the amount of polymer was almost negligible. When the oxidizing potential was increased the molecule appeared to suffer complete disintegration (60).

When β pinene was oxidized in a saturated solution of sodium bicarbonate using a platinum anode, β pinene disappeared but in general no oxidation product could be isolated from the remaining liquid except polymer. Control experiments where no electricity was passed produced no reaction and indicates that the β pinene which could not be accounted for was completely oxidized to CO_2 . In one experiment however, the electrode potential was much below that usually attained. The platinum anode was brown at the conclusion of the oxidation and nopinone was isolated and identified by its semicarbazide. The physical properties of this derivative were quite similar to those described in chapter II. Duplicate runs did not give nopinone and it is thought that a trace catalyst or "oxygen Carrier" was responsible for the change in the course of the oxidation.

Since β pinene appears to be completely oxidized at a platinum anode the lead dioxide anode in 10% sulfuric acid was tried. The β pinene was isomerised to α pinene and to dipentene. Hydration products were terpeneol and 1-8 terpin. Oxidation products were terebic acid and a polymer.

Sodium bicarbonate was substituted as the electrolyte to reduce the oxidation potential and beta pinene gave as oxidation products, polymer and pinocarvone. Pinocarvone was identified by its semicarbazone.

Hydration and isomerization products were negligible.

Hydration Experiments

In table VIII experiments 14 and 15, page 78, give the action of the electrolyte on the β pinene.

When 10% sulfuric acid is stirred with β pinene under conditions of the electrolytic oxidation except that no current is passed through the emulsion, the hydration products α terpineol and 1-8 terpin hydrate were formed. The time was about the same as in the electrolytic oxidations and was about 100 hours.

The amount of polymerization is small.

Since the above products would be formed by hydration in a sulfuric acid medium, it was necessary to find a medium that would keep hydration products to a minimum in order to study the action of electricity on pure β pinene.

Sodium bicarbonate emulsions were used to give neutral solutions and one that was not likely to cause hydration. The action of saturated sodium bicarbonate emulsions on β pinene is given in table VIII, page 78. It is seen that both hydration and isomerization products are negligible.

Identification of Products

The hydrocarbons α pinene, β pinene and dipentene and the ketones pinocarvone and nopinone had similar properties to those described in Chapter II and were analyzed and identified in the same manner.

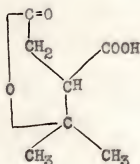
Terpineol had the following constants: b.p. 112° (20 mm), d^{25}_4 0.930, n^{25}_D 1.4810, $(\alpha)^{25}_D$ -80° . Stephan (53) gives: b.p. $219-221^{\circ}$ (760 mm), d^{15} 0.938, n^{15}_D 1.48322, (α) -95.5° . Fuller and Kenyon (20) reported: b.p. 104° (15 mm), $d^{14.5}_4$ 0.9475, n^{15}_D 1.4819, $(\alpha)^{20}_D$ -100.5° . It was identified by its phenylurethane m.p. $107-8^{\circ}$. Kay and Perkin (27) reported 109.5° .

Cis-terpin hydrate was identified by its m.p. of $112-113^{\circ}$. When mixed with a known sample of cis-terpin hydrate the melting point was still $112-113^{\circ}$. Bayer (4) gives $116-117^{\circ}$ for cis terpin hydrate and $104-105^{\circ}$ for cis-terpin. The anhydrous glycol on exposure to air rapidly adsorbs water with the formation of the hydrate.

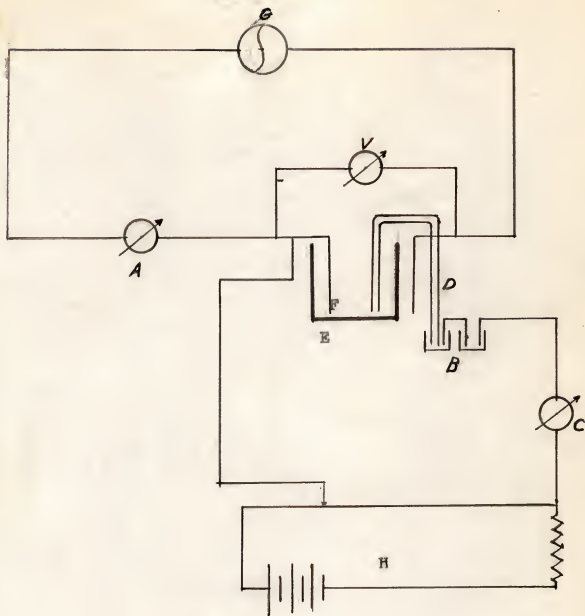
The mixtures of tri- and tetra-acetates were determined by hydrolysis constants only and the

alcohols were not isolated. These acetates were hydrolyzed by heating them with an excess of KOH in ethylene glycol and back titrating with standardized HCl.

Terebic acid, XIV, was identified by its melting point of $172-174^{\circ}$ and its neutral equivalent of 84. The calculated neutral equivalent for $C_7H_{10}O_4$ is 81. The accepted (30) value for the melting point is $174-175^{\circ}$.



XIV



- A Ammeter
- B Calomel half cell
- C Galvanometer
- D Agar-agar KCl bridge
- E Reaction Cell
- F Anode
- G D.C. generator
- H Student potentiometer
- V Voltmeter

Fig. 6 Electrical Connections for
Electrolytic Oxidations

TABLE VIII
Data on the Electrolytic Oxidation of Beta Pinene

Experiment No.	Weight of pinene	Electrode composition	Anolyte	C.D. am/cm ²	Faradays per mol	Electrode potential	Temperature degrees C
1	85 g	platinum	H ₂ O-NaCl water	0.00032	1.61	--	25-38
2	100 g	"	" "	0.0004	2.8	--	2-15
3	100 g	PbO ₂ on Pb	10% H ₂ SO ₄	0.0030	11.2	1.90 volts	26-28
4	100 g	" "	" "	0.0025	6.4	1.80	24-30
5	200 g	Platinum	Sat NaHCO ₃	0.00083	3.9	2.3	23-35
6	200 g	"	" "	0.0010	4.6	2.4	23-35
7	190 g	"	" "	0.0021	6.0	1.9	25-32
8	200 g	"	" "	0.0021	6.8	2.7	28-34
9	100 g	"	" "	0.0019	14.0	2.2	35-38
10	136 g	"	" "	0.0031	14.0	2.8	30-32
11	136 g	"	10% H ₂ SO ₄	0.0019	9.2	3.1	25-48
12	150 g	"	" "	0.0025	3.3	3.2	20-22
13	50 g	PbO ₂ on Pb	Sat NaHCO ₃	0.0019	3.0	1.26	25-28
14	100 g	" "	" "	0.0020	6.8	1.28	25-28
15	100 g	--	10% H ₂ SO ₄	--	--	--	25.0
16	100 g	--	Sat NaHCO ₃	--	--	--	25-30

TABLE VIII

Data on the Electrolytic oxidation of Beta Pinene

Experiment No.	% α pinene	% β pinene	% Dipentene	% terpineol	% 1-8 cis-terpin
1	--	--	--	12	35.6
2	--	--	--	--	52.8
3	--	--	8.3	9.2	28.6
4	--	9.2	8.0	10.9	36.2
5	--	62	--	--	--
6	--	75	--	--	--
7	--	68.5	--	--	--
8	--	52.0	--	--	--
9	--	16.0	--	--	--
10	--	84	--	--	--
11	3.0	13.6	--	4.4	--
12	4.7	61.3	14.8	1.3	1.1
13	--	52	6	--	--
14	--	43	8.0	--	--
15	2.2	81.2	3.4	2.3	--
16	--	92	--	--	--

TABLE VIII

Data on the Electrolytic Oxidation of Beta Pinene

Experiment No.	% tri- and tetra- acetate	% terpineol acid	% nopinone	% pinocarvone	% polymer	% Recovery
1	10.8	--	--	--	5	63.4
2	12.6	--	--	--	9	74.4
3	--	12.2	--	--	14.1	81.1
4	--	8.1	--	--	9.0	81.4
5	--	--	--	--	12	74.0
6	--	--	--	--	10	85.0
7	--	--	10.5	--	5.3	84.3
8	--	--	--	--	7.5	59.5
9	--	--	--	--	14.4	30.0
10	--	--	--	--	4.4	88.4
11	--	10.1	--	--	11.0	42.1
12	--	--	--	--	8.3	91.5
13	--	--	--	6	10	74.0
14	--	--	--	9	14	74.0
15	--	--	--	--	1.0	90.1
16	--	--	--	--	--	92.0

Discussion

The results of Fichter and Schetty have been duplicated except that no p-cymene or cineol were obtained. It has been pointed out, however that there was a possibility that the p-cymene and cineol were present in the pinene used by them since both are natural products of turpentine.

It has been shown by Tommila (60) that the material obtained is dependent upon the anode material. Some anodes oxidize the compound leaving the chain intact while bright platinum tends to break the C-C bond to give CO₂. This has been verified in that pinene disappears when electrolyzed at a bright platinum electrode.

When the electrode potential was lowered by the use of the lead dioxide electrodes terebic acid was obtained, which is in conformity with the theoretical discussion already given. Beta pinene in a sodium bicarbonate solution at a lead dioxide anode gave pinocarvone and a polymer.

Other important factors that must be more rigidly controlled than have been possible at this laboratory are the current density, temperature, and the anolyte purity. The motor generator set was run from a

110 volt A.C. outlet. This source of current was observed to vary from 100 volts to 128 volts, which of course, caused the output from the direct current generator to vary as much as 25% from any given setting. While the temperature in the catholite remained within 0.5° of that set by the thermoregulator the temperature inside the cup would vary as much as 8° because of the different amount of current passing through it. Since it has been shown that an increase in temperature caused reactions to proceed more easily and because of the increased overvoltage from the increased current density, the reactions could not be controlled as accurately as was necessary for quantitative work in this field. The clay cups were not analyzed for mineral content and sometimes there seemed to be some minerals introduced into the anolyte that acted as catalyst.

The problem of electrolytic oxidation is a science but at the present time it has not been developed much beyond the stage of an art. When the process is placed on a sound foundation it should prove to be one of the most versatile method of oxidation known. The correct control of the electrode potential, the current density, anolyte composition, anode material and temperature, should make it versatile

enough to accomplish any oxidation that is now possible by chemical means and many that are not today possible.

Summary

Pinene was oxidized in acetic acid with a platinum anode and mixtures of tri- and tetra-acetates were formed.

The anode potential of platinum is so high in 10% sulfuric acid solution that β pinene is apparently completely oxidized.

In one experiment using a platinum anode and saturated sodium bicarbonate anolyte nopinone was obtained.

Separate experiments show that beta pinene is hydrolyzed to terpineol and terpin hydrate in 10% sulfuric acid when no electricity is passed.

With a 10% sulfuric acid anolyte and lead dioxide anode, β pinene was oxidized to terebic acid. These compounds terpineol and 1-8 terpin obtained by Fichter and Schetty (17) were shown definitely to be hydration products.

With a lead dioxide anode and a saturated bicarbonate anolyte, β pinene gave pinocarvone. Hydration of the β pinene was negligible.

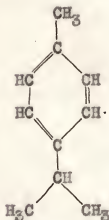
Temperatures, current densities, and anode potentials are recorded. The anode potential is greater when measured from the top of the anolyte to the anode than when measured from the bottom. Stirring had no effect on the potential.

Chapter IV

THE OXIDATION OF CYCLOHEXENE

Introduction

Fichter and Schetty (17) reported p-cymene from the electrolytic oxidation of pinene. p-Cymene, XV, could be formed by the dehydrogenation of beta pinene, I.



XV

Since p-cymene would be present as a dehydration product, it was decided to oxidize cyclohexene electrolytically to see whether adipic acid or benzene, or both, would be formed. The benzene would be a dehydrogenation product, while adipic acid would form by the fission of the ring at the ethylenic linkage.

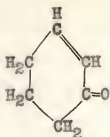
Preparation of Cyclohexene

The cyclohexene was prepared by allowing commercial cyclohexanol to drip into phosphoric acid at 140°. The phosphoric acid dehydrated the cyclohexanol and the cyclohexene was distilled out as it was formed. Yields were 92-95% based on cyclohexanol. The cyclohexene was separated from the water that distilled over and dried over sodium for a day. The cyclohexene was fractionated and had the following constants; b.p. 83.3 (760 mm), d_{25}^{25} 0.806, n_D^{25} 1.4443. These are the accepted constants (30).

Electrolytic Oxidation

50 g of cyclohexene were oxidized at a lead dioxide anode in a saturated sodium bicarbonate emulsion at 25-30°. The electrode potential was 1.26 volts and the current density was 0.0021 amperes per square centimeter. The equipment was the same as used for the electrolytic oxidation of β pinene. 5.2 Faradays per mol of cyclohexene were passed through the emulsion.

No acids were present. The mixture was extracted with ether and carefully fractionated. No benzene could be detected. 4 g of cyclohexene-1,one-3, XVI,



XVI

were collected, and had the following constants; b.p. 64-65 (20 mm), n_D^{25} 1.4808, d_4^{25} 0.965. It was identified as its semicarbazone m.p. 164-166°. Marvel and Walton (34) reported; b.p. 67-69 (22 mm), n_D^{20} 1.4818 and a semicarbazone m.p. of 160-161°.

The only other recovery was 4 g of polymer that was insoluble in the common solvents. The total recovery was only 16%.

Other experiments under the same conditions except for an ice trap outlet for minimizing evaporation losses gave from 74 g of cyclohexene 37% polymer and 21% cyclohexene-1, one-3. Physical constants were similar to those above.

Selenium Dioxide Oxidation of Cyclohexene

It has been shown that selenium dioxide attacks a methyl or methylene group activated by an ethylenic linkage to form unsaturated alcohols and ketones (54).

Since cyclohexene-1,one-3, described above, is obtained by the oxidation of a methylene group activated by an ethylenic linkage, cyclohexene was oxidized by selenium dioxide in order to compare the action of selenium dioxide to electrolytic oxidation under the conditions described above.

Preparation of Selenium Dioxide

Selenium of 99% purity was dissolved in an excess of concentrated nitric acid in the hood. This solution was then evaporated to dryness over a steam bath. When dry it was dissolved in water, filtered and again evaporated to dryness. It was again dissolved in water filtered and evaporated. When dry it was heated at 125° for 4 hours and pulverised in a Mortar. When prepared in this manner (57) the product was quite free from nitric acid and ready for use.

Experimental

The cyclohexene was placed in a three neck flask equipped with a stirrer and a reflux condenser and a plug for adding the powdered selenium dioxide. The powdered selenium dioxide was added slowly. Care must be taken to avoid too rapid an addition as this

will cause the reaction to take place with explosive violence. It was added at such a rate that the temperature was about 50°. When all the selenium dioxide was added the mixture was refluxed for four hours. The molar ratio of selenium dioxide to cyclohexene was 1 : 1.

This mixture was steam distilled and from 82 g of cyclohexene, 14 g of cyclohexene-1,one-3 were obtained. It was identified as previously described.

About 0.8 g of cyclohexene-1,ol-3 was fractionated from the above steam distillate. It had the following constants; b.p. 74-75 (20 mm), n_{D}^{25} 1.4720, d_4^{25} 0.98. It was identified as its phenylurethane, m.p. 102-104°. Marvel and Walton (34) reported 106-107° as the melting point of the phenylurethane.

Conclusion

It has been shown that under certain conditions that electrolytic oxidations parallel the action of selenium dioxide.

Summary

Cyclohexene was oxidized by electricity at a lead dioxide anode in saturated sodium bicarbonate emulsion and by selenium dioxide. Both yielded cyclohexene-1,one-3. From the selenium dioxide oxidation a small amount of cyclohexene-1,ol-3 was isolated. It was characterized.

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BIOGRAPHICAL ITEMS

James Beverly Redd was born December 21, 1918 at Perry, Florida. He attended the public schools of Union County and Leesburg (Florida). He has attended the University of Florida since 1936, where he received the degree of Bachelor of Science in 1940.

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COMMITTEE REPORT

This dissertation was prepared under the direction of the Chairman of the candidate's Supervisory Committee and has been approved by all members of the Committee. It was submitted to the Graduate Council and was approved as partial fulfilment of the requirements for the degree of Doctor of Philosophy.

Date August 27, 1943

J. H. Norman
Acting Dean

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